PH TREATMENT OF POME VIA BIOLOGICAL PROCESS – OPTIMIZATION

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ABSTRACT

Palm oil mill effluent (POME) has been known as organic waste product from palm oil production which is featured by low pH of 3.5-4.5, high value of biological demand (BOD), chemical oxygen demand (COD) and suspended solids. It is found that palm oil industry is one of the contributors of environmental pollution if their waste not being treated well. So, it is mandatory for all palm oil mills to treat their wastewaters on site to an acceptable level before it is allowed to be discharged into the water courses. Biological treatment appears less cost than chemical and physical methods, and also much faster than natural oxidation, with a lower environmental impact. Thus, this study is aims to optimize the factors which are influencing biological pH treatment of acidic POME by using research surface methodology (RSM) with CCD response of Design Expert software via biological treatment of using soil mixed culture. In the beginning, the sample of acidic POME was collected from a nearby palm oil mill whereas soil mixed culture was obtained from soil near to plants root system. Preliminary study to obtain the best reaction time was done in 5th days and at the end, the utilization was performed better in between 3^{rd}-4^{th} days. Then, an acclimatization of soil mixed culture together with POME was conducted and 13 experimental runs were done according to RSM. Lastly, all the experimental results data will be optimized using RSM with factorial central composite design (CCD) using the software package Design Expert Version 6.0. The model showed that pH will increase upon increasing of agitation and temperature between to optimum conditions, but declined with further increases of these factors. From these optimum condition, it can be concluded that agitation and temperature had an individual significant influence on pH. Yet, the agitation and temperature was interdependent or having significant interaction on pH treatment while pH and temperature were interdependent according to the study and slightly interdependent and their interactive effects were insignificant. Based on the results, the predicted optimum condition suggested by software is temperature of 32.50℃ and agitation speed of 125 rpm. The expected pH value of 8.03 may obtained. Thus, the experimental response variables were very close to those predicted by RSM, indicating that RSM was a useful tool to optimize the pH treatment. Besides, the error generated was 2.293% indicated that the data was valid since the result does not excess 10%. After all, it can be concluded that the agitation speed and temperature were optimized to the optimum conditions and can be applied in industrial applications.

ABSTRAK

Sisa minyak kumbahan kilang kelapa sawit telah dikenali sebagai bahan buangan organik daripada pengeluaran minyak sawit yang dicirikan seperti pH rendah diantara 3.5-4.5, mempunyai nilai tinggi keperluan oksigen biokimia (BOD), keperluan oksigen kimia (COD) dan pepejal terampai. Industri minyak sawit adalah salah satu daripada penyumbang pencemaran alam sekitar jika sisa mereka tidak dirawat dengan baik. Jadi, ia adalah wajib untuk kilang-kilang minyak sawit bagi merawat air buangan mereka ke tahap yang boleh diterima sebelum ia dibenarkan untuk dilepaskan ke dalam saluran air. Kebanyakan menggunakan rawatan biologi kerana kurangnya kos yang diperlukan daripada kaedah kimia dan fizikal, dan juga lebih cepat daripada pengoksidaan semula jadi, dengan kesan alam sekitar yang lebih rendah. Oleh itu, kajian ini adalah bertujuan untuk mengoptimumkan faktor yang mempengaruhi rawatan pH biologi POME berasid dengan menggunakan kaedah permukaan sambutan (RSM) dengan rekaan komposit pusat (CCD) menggunakan pakej perisian ‘Design Expert’ versi 6.0 melalui rawatan biologi menggunakan tanah pelbagai kultur. Pada mulanya, sampel POME berasid dikumpulkan dari kilang minyak sawit yang berhampiran manakala tanah pelbagai kultur telah diperolehi daripada tanah berhampiran sistem akar. Kajian awal untuk mendapatkan tindak balas masa yang terbaik telah dilakukan selama 5 hari dan pada akhirnya, keputusan eksperimen lebih baik adalah di antara hari ke-3-4. Kemudian, satu penyesuaian tanah pelbagai kulttur bersama-sama dengan POME telah dijalankan dan 13 eksperimen telah dilakukan mengikut RSM. Akhir sekali, semua keputusan data eksperimen akan dioptimumkan menggunakan RSM dengan reka bentuk CCD menggunakan pakej perisian Design Pakar Versi 6.0. Model telah menunjukkan bahawa pH akan meningkat apabila meningkatnya kelajuan putaran dan suhu hingga antara keadaan yang optimum, tetapi menurun dengan kenaikan lebih daripada faktor-faktor ini . Dari nilai optimum ini, ia boleh disimpulkan bahawa kelajuan putaran dan suhu mempunyai pengaruh besar ke atas pH. Namun, kelajuan putaran dan suhu adalah saling bergantung atau mempunyai interaksi yang ketara ke atas rawatan pH manakala pH dan suhu telah saling bergantung menurut kajian dan sedikit saling bergantung dan kesan interaktif mereka juga tidak ketara. Berdasarkan kepada keputusan , keadaan optimum yang diramalkan dicadangkan oleh perisian adalah suhu 32.50 ℃ dan kelajuan pergolakan 125 rpm. Jangkaan nilai pH 8.03 boleh diperolehi. Oleh itu, nilai pemboleh ubah tindak balas eksperimen sangat hampir dengan yang diramalkan oleh RSM, menunjukkan RSM adalah cara yang berguna untuk mengoptimumkan rawatan pH. Selain itu,

ralat yang dihasilkan adalah 2.293% menyatakan data itu adalah sah kerana ianya tidak melebihi 10%. Kesimpulannya, ia dapat disimpulkan bahawa kelajuan putaran dan suhu telah dioptimumkan untuk keadaan optimum dan boleh digunakan dalam aplikasi industri.

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LIST OF ABBREVIATION

AN	Ammonia Nitrogen
BBD	Box-Behnken Design
BOD	Biochemical Oxygen Demand
Ca	Calcium
CCD	Central Composite Design
COD	Chemical Oxygen Demand
CPO	Crude Palm Oil
CV	Coefficient Variations
DOE	Department of Environment
DoE	Design of Experiment
EQA	Environmental Quality Standard
FD	Factorial Design
FFB	Fresh Fruit Bunch
GDP	Gross Domestic Product
K	Potassium
Mg	Magnesium
MPOB	Malaysian Palm Oil Board
N	Nitrogen
P	Phosphorus

POME	Palm Oil Mill Effluent
RSM	Research Surface Methodology
SS	Suspended Solids
TN	Total Nitrogen
TS	Total Solids
TVS	Total Volatile Solids
VFA	Volatile Fatty Acids

TABLE OF NOMENCLATURE

F	Flow rate	tonnes/hr
t	Reaction time	min, s
V	Volume	m^3, mL
P	Pressure	Pa
T	Temperature	°C
m	Mass	tonnes, kg
c	Concentration	mg/L
s	Agitation speed	rpm

1 INTRODUCTION

1.1 Research Background

The Malaysian palm oil industry has seen as a new growth in the last four decades to emerge as the leading agricultural industry in the country. Palm oil was first introduced to Malaysia in year 1875 as an ornamental plant (Lang, 2007). Furthermore, palm oil is one of the main agricultural products of Malaysia which constitutes 41.37% of total world production for the year 2007 (Malaysian Palm Oil Board (MPOB), 2009). Currently, about half of the agricultural land in Malaysia is conquered by palm oil and the area is expanding. In 2003, more than 3.79 million hectares of land were under oil palm cultivation, occupying more than one-third of the total cultivated area in Malaysia and 11% of the total land area (Wu *et al*., 2009). Nowadays, Malaysia is the world's biggest producers and exporters of palm oil. The palm oil industry is primarily export-oriented. As cited by Wu *et al*. (2010), the amount of export earnings from palm oil, palm kernel oil and associating products in 1998 is almost US$5.6 billion, equivalent to 5.6% of the gross domestic product (GDP).

Moreover, palm oil has unique composition which makes it various in its application in food manufacturing and in the chemical such as manufacture of cleaning products, cosmetic and pharmaceutical industries. Its semi-solid physical properties are required in much food preparation, for example, being used as an ingredient in a wide range of foods including biscuits, bakery products, snacks and ice-cream. Animal feed may also contain palm oil and palm kernel meal. Besides, its non-cholesterol quality and digestibility make it popular as source of energy such as fuel, while its technical and economic superiority makes it preferable as base material in the manufacture of various non-edible products.

1.2 Motivation and problem statement

While it is recognized that the revenue from palm oil industry has contributed much towards the national development and improvement in the standard of the living of the people, the rapid expansion of the industry has also contributed to the environmental pollution. Oil palm cultivation and processing like other agricultural and industrial activities will raise environmental issues (Mustapa, 2008). Other than that, the palm oil mill industry in Malaysia is identified as the one contributing the largest pollution load in rivers throughout the country (Wu *et al*., 2010). An increasingly stringent environmental regulations in view of the government's commitment to the conservation of the environment and increased public awareness of pollution problems caused the palm oil industries facing tremendous challenges as palm oil mill effluent (POME) is a highly pollutant effluent. POME treatment requires an efficient system in facing the current challenges. There are many processing plants failed to achieve the standard discharge limits. It is mandatory for all palm oil mills to treat their wastewaters on site to an acceptable level before it is allowed to be discharged into the water courses.

There are many current treatment methods, which are adopted by the palm oil industries. Currently, the ponding system is the most common treatment employed by most of the palm oil mills as their conventional treatment of POME (Wu *et al*., 2010) but other processes such as aerobic and anaerobic digestions, physicochemical treatments and membrane filtrations can provide the palm oil industries with a possible insight into the improvement of current POME treatment processes (Wu *et al*., 2009). On the other hand, the treatment that is based mainly on biological treatments of anaerobic and aerobic systems is quite inefficient to treat POME, which unfortunately leads to environmental pollution issues (Wu *et al*., 2009). This is because the high BOD loading and low pH of POME, together with the colloidal nature of the suspended solids, renders treatment by conventional methods difficult (Wu *et al*., 2009). A new and improved POME treatment would be required in order to meet the requirements of Department of Environment (DOE) discharge limits in order to increase the efficiency of biological methods used.

Although there has been successful industrial-scale of palm oil mill effluent treatment, generally the industry is still facing various challenges to ensure the standards for POME discharge into watercourses is achieved. Otherwise, this study was focusing on the pH where the pH of POME also plays an important role to make the effluent can be discharge. If pH of POME is not achieved the standards outlined by POME discharge standards under the Environmental Quality Act of Malaysia, 1974 it will not discharged or will cause the environmental pollution. In the Environmental Quality (Prescribed Premises) (Crude Palm Oil) (Amendment) Regulations 1982, the pH limits for POME discharge is between 5 and 9. Hence, this study will optimize the factors that can increase the pH from the previous study by using biological pH treatment. The pH changes can be influenced by many factors. These factors included agitation speed, temperature, and reaction time.

1.3 Objective

This work aims to optimize the factors which are influencing biological pH treatment of acidic POME.

1.4 Scope

To achieve the objectives of this research, the main research fields to be carried on which are;

- By using soil mixed culture.
- To acclimatize the POME and soil mixed culture to be inoculums.
- To analyze pH of POME sample after the treatment with soil mixed culture.
- To optimize the factors which are agitation speed, temperature and reaction time by using research surface methodology (RSM) with CCD response via Design Expert software.

2 LITERATURE REVIEW

2.1 Overview

This chapter provides a brief review that relating with this study. First of all, the review explains the palm oil mill processing for producing POME from CPO, the characteristics of POME, and the Enactment of Environmental Quality Act for discharging POME. Secondly, the review covers about the biological method involved in the treatment process; aerobic and anaerobic treatment processes of POME, inoculums used and factor that affecting biological pH treatment. Finally, the design of experiment using response surface methodology which was applied in this research to model and optimize the process is also elaborated.

2.2 Palm oil mill processing and process description

The wet palm oil milling process is the most standard and distinctive way of extracting palm oil, especially in Malaysia. In large factories, steam and water are used, thus giving rise to the wastewater known as palm oil mill effluent (POME). The palm oil milling process is more or less the same for all the mills throughout the country (Wu *et al*., 2010). The stages involved in the typical processing of crude palm oil (CPO) are depicted in Figure 2.1. The three main sources of POME are steriliser condensate, hydrocyclone waste and clarifier sludge. For a well-controlled conventional oil palm mill, about 0.9 m^3, 0.1 m^3 and 1.5 m^3 of steriliser condensate, clarifier sludge and hydrocyclone waste are generated for each tonne of crude palm oil produced (Lang, 2007).

CPO is extracted from the mesocarp of fresh fruit bunch (FFB). The capacity of a large scale mills range from 10 to 60 tonnes FFB/h. The first step consists in sterilizing the FFB in steam sterilizers for 50 min at about 140 ℃ and a pressure of 3 x 10^5 Pa in order to stop the rapid formation of free fatty acids during the pulping process. This process also allows the fruits that are still attached in bunch to be loosened. Secondly, the stripping is to separate the sterilized fruits from the bunch stalks by using a rotary drum thresher. The fruit are then mashed in the digester under steam heated condition with temperature around 90℃. Twin screw presses are generally used to press out the oil from the digested mashed fruits under high pressure. The oil is thus separated from the spent mesocarp and the nuts. But then, the crude oil extracted from digested palm fruit contains varying amounts of water as well as impurities consisting of vegetable matter. This matter is in the form of either insoluble solids or dissolved matter in water. By settling and centrifuging, the water present in the crude oil can be largely removed from the ‘bottom’ phase since most of it is free or non-dissolved. The ‘bottom’ phase of the clarification or settling tank is sent to a sludge separator or centrifuge where approximately 1.5 tonnes of sludge waste is obtained per tonnes of produced crude palm oil. During pressing of the digested fruit to extract the oil, a cake made up of nuts and fiber is produced. After separation of the fiber from the nuts, the latter are sent for further processing from which another product, the palm kernel is obtained. This processing section is constituted of a hydrocyclone that separates the kernels from the empty shells after cracking the nuts. Approximately 0.1 tonnes of liquid effluent per tonnes of produced crude palm oil is generated in this process. Any uncracked nuts must be removed and recycled, and the shell separated from the kernels. The kernel is dried to below 7% moisture in order to prevent the growth of mould for a longer storage time.

2.3 Crude palm oil (CPO)

The production of such large amounts of CPO results in even larger amounts of POME. For each tonne of CPO produced from the fresh fruits bunches, approximately 6 tonnes of waste palm fronds, 5 tonnes of empty fruit bunches, 1 tonne of palm trunks, 1 tonne of press fibre (from the mesocarp), 500 kg of palm kernel endocarp, 250 kg of palm kernel press cake, and 100 tonnes of POME can be obtained (Foo & Hameed, 2010). Table 2.1 show that the total productions of CPO for the month of January-February 2012 and 2013 respectively. Approximately 2.9 million tonnes of CPO was produced in the month Jan-Feb in 2013 which increased by 14.54% from 2.47 million tonnes in the month Jan-Feb in 2012 (MPOB, 2013). The production of POME has been increased lately due to the demand for palm oil in the world at an average rate of 7.36% per year during 2006-2010 (Yossan *et al.*, 2012).

Table 2.1: Malaysian production of CPO in Jan-Feb 2012 and 2013

States	Jan – Feb Total	
	2012	2013
Johor	372,928	417,141
Kedah	43,769	45,824
Kelantan	30,886	39,617
Melaka	16,185	13,447
Negeri Sembilan	85,082	102,397
Pahang	339,483	420,334
Perak	264,496	287,523
Pulau Pinang	14,206	15,404
Selangor	89,916	85,785
Terengganu	57,954	63,975
Sabah	779,710	979,533
Sarawak	382,035	427,088
Total	2,476,650	2,898,068

(Source: MPOB, 2013)

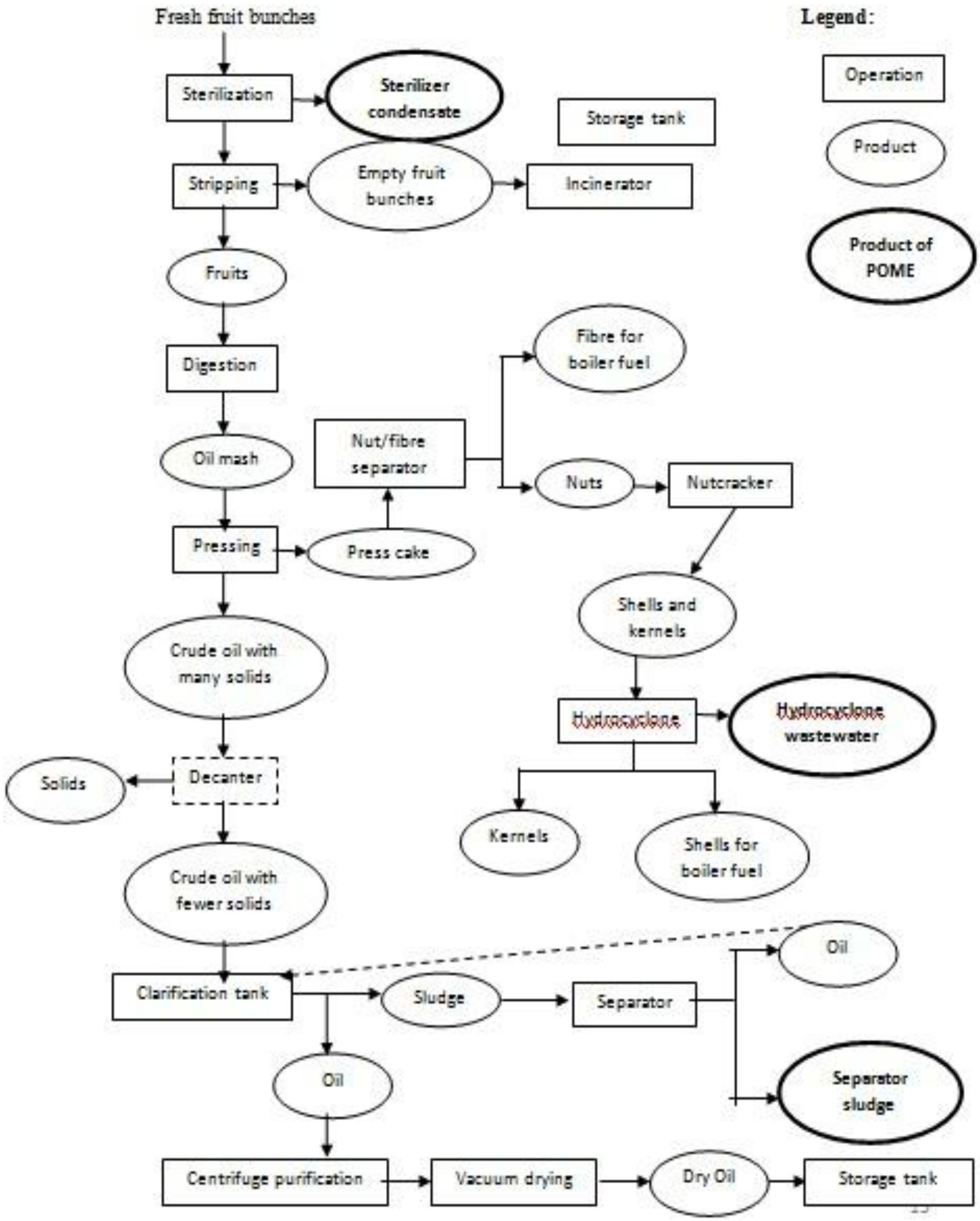

Figure 2.1: Process operations and products in a typical palm oil milling process

(Source: Wu *et al*., 2010)

2.4 *Palm Oil Mill Effluent (POME)*

POME is a type of organic waste which consists of a significant amount of solid wastes and wastewater (cellulosic material, fat, oil and grease etc) produced by palm oil industry during milling process. By nature, fresh POME is an acidic, thick, brownish, viscous and voluminous colloidal suspension with 95-96% of water, 0.6-0.7% of oil and 2-4% suspended solids. It also contains an essential inorganic nutrients (sodium, potassium, calcium, magnesium, manganese, and iron), cell walls, organelles, and short fibres, a range of nitrogeneous compounds from proteins to amino acids, free organic acids and a spectrum of carbohydrates ranging from hemicelluloses to simple sugars. Besides, raw POME is featured by low pH value of 3.5-4.5, high biological oxygen demand (BOD) of 10, 250-43,750 mg/L, chemical oxygen demand (COD) of 16,000-100,000 mg/L, suspended solids of 5000-54,000 mg/L, nitrogen content ranging from 200 to 500 mg/L as ammonia nitrogen and total nitrogen and discharge temperature of 80-90℃ (Foo & Hameed, 2010).

It can be seen in the Table 2.2, that the BOD: COD ratio of raw POME is approximately 1:2 which means that POME is considered to be suitably treated by biological processes. While the typical BOD: N: P ratio of 139: 4: 1 indicates the limitations of nutrient, which is required for bacterial growth and metabolic requirements of biomass to obtain optimum biological processes under aerobic conditions, which requires 100: 5:1. Nutrient deficiency can lead to increase the population of filamentous bacteria (Ujang & Lim, 2004).

Generally, the characteristics of POME may change substantially for different batches, days and factories; depend on the processing techniques, the age or type of fruit, the discharge limit of the factory, climate and condition of the palm oil processing as cited by Wu et al. (2010). Seasonal oil palm cropping, palm oil mill activities (such as occasional public holidays, closure of the mill, operation and quality control of individual mills) will also influence the quality and quantity of the discharge POME which in turn affect the biological treatment process of POME. Thus, the variation of treatment of POME in palm oil industries has been selected depending on the several of characteristics of POME, in terms of quality and quantity.

Table 2.2: Palm Oil Mill Effluent (POME) characteristics

GENERAL PARAMETERS		
PARAMETER*	MEAN	RANGE
pH	4.2	3.5-5.2
Oil & Grease	6,000	150-18,000
Biochemical Oxygen Demand (BOD)	25,000	10,000-44,000
Chemical Oxygen Demand (COD)	50,000	16,000-100,000
Total Solids (TS)	40,500	11,500-79,000
Suspended Solids (SS)	18,000	5,000-54,000
Total Volatile Solids (TVS)	34,000	9,000-72,000
Ammonia Nitrogen (AN)	35	4-80
Total Nitrogen (TN)	750	80-1,400
Phosphorus	180	
Magnesium	615	
Calcium	440	
Boron	7.6	
Iron	47	
Manganese	2.0	
Copper	0.9	
Zinc	2.3	

*All parameters in mg/L except pH

(Source: Industrial Processes & The Environment (Handbook No.3) - Crude Palm Oil Industry, 1999)

2.5 Environmental Quality Standard

With the rapid expansion of the palm oil industry and the public's increased awareness of environmental pollution, the industry is compelled both socially and aesthetically to treat its effluent before discharging it. After the enactment of the Environmental Quality Act (EQA), 1974 and the establishment of the Department of Environment in 1975, comprehensive environmental control of the crude palm oil industry was commenced. The Environmental Quality (Prescribed Premises) (Crude Palm Oil) Order, 1977 and the Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulations, 1977 were proclaimed under the EQA, in order to regulate the discharge of effluent from the crude palm oil industry as well as to exercise other environmental controls (Pierzynski *et al.*, 2005). These were the first sets of industry specific subsidiary legislation to be proclaimed under the EQA for industrial pollution control. Table 2.3 presented the current effluent discharge standard ordinarily applicable to crude palm oil mills.

Table 2.3: Prevailing effluent discharge standard for CPO mills

Parameters	Unit	Parameter Limits
Biochemical Oxygen Demand (BOD) (BOD; 3 days, 30 ℃)	mg/L	100
Chemical Oxygen Demand (COD)	mg/L	*
Total Solids (TS)	mg/L	*
Suspended solids (SS)	mg/L	400
Oil & Grease (O&G)	mg/L	50
Ammonia Nitrogen (AN)	mg/L	150
Total Nitrogen (TN)	mg/L	200
pH		5-9
Temperature	℃	45

*no discharge standards after 1984

(Source: Pierzynski *et al.*, 2005)

2.6 Effects of acidic pH of POME

As mentioned earlier, Malaysia is identified as the country that produces the largest pollution load in the river. Even though POME is considered as non toxic, but it is identified as a major source of aquatic pollution by depleting dissolved oxygen when discharged untreated into water bodies. The acidity of POME has important consequences on the survival of aquatic organisms if it not being treated well. Acid pH levels can be harmful to fish, invertebrates, and other water organisms that are affected either directly or indirectly by acidic substances. The low pH can result in lakes, streams, and rivers that no longer support aquatic life.

Other than that, land application of POME is one of the disposal alternatives; however, it must be disposed by controlling of small quantities of POME at a time to avoid clogging and water logging of soil and kills the vegetation on contact (Wood *et al*., 1979). As discussed by Iwara *et al.* (2011), the low pH of raw POME will increase to near neutrality in soil as biodegradation takes place. This therefore, implies that POME increases soil pH which in effect increases the values of major nutrients (nitrogen (N), potassium (K) and phosphorus (P)) in the soil since POME also contains appreciable amounts of N, P, K, magnesium (Mg) and calcium (Ca), which are the vital nutrient elements for plant growth.

2.7 Biological treatment of POME

In biological treatment, microorganisms use the organics in wastewater as a food supply and convert them into biological cells, or biomass. Because wastewater contains a wide variety of organics, a wide variety of organisms, or a mixed culture, is required for complete treatment. Each type of organism in the mixed culture utilizes the food source most suitable to its metabolism.

Biological treatment of POME has been widely studied. Biological treatment appears less cost than chemical and physical methods, and also much faster than natural oxidation, with a lower environmental impact. The common biological processes that being used for treatment of waste products is aerobic treatment process and anaerobic treatment process.